

1172,931



## PATENT SPECIFICATION

PCX/D2

NO DRAWINGS

1172,931

Date of Application (No. 5042/67) and filing Complete Specification: 2 Feb., 1967.

Application made in United States of America (No. 527,109) on 14 Feb., 1966.

Complete Specification Published: 3 Dec., 1969.

Index at acceptance:—C3 R27K8F; C5 D(6A5D1, 6A5D2, 6A5E, 6B12N1, 6C6)

International Classification:—C 08 g 23/10

## COMPLETE SPECIFICATION

### Improvements in or relating to Nonionic Condensation Products

We, MARLES-KUHLMANN-WYANDOTTE, a French body corporate of 25, Boulevard de l'Amiral Bruix, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new non-ionic condensation products for use in automatic dishwashing machines. More particularly, the invention relates to certain biodegradable "heteric" alkylene oxide condensation products which are particularly efficacious when employed in automatic dishwashing machines.

Machine dishwashing compositions generally are formulated from inorganic salts such as sodium tripolyphosphate, alkaline builders such as sodium metasilicate, chlorinated inorganic compounds such as chlorinated trisodium phosphate, and surface active agents such as ethoxylated alcohols and alkyl phenols. In these compositions, the surface active agent generally functions as a wetting agent, foam suppressant and auxiliary cleaning agent. In addition to possessing the properties which allow these agents to function in the above-stated manner, another requirement of surface active agents is that they be biodegradable. More recently, surface active agents, to be useful in automatic dishwashing compositions, are required to suppress the generation of foam at temperatures as low as 100° F. Although at first blush the latter requirement appears arbitrary, it has been determined that a considerable amount of automatic dishwashers operate at or near this temperature. None of the surface active agents presently used in dishwashing compositions have been found to suppress foam at this temperature.

Another use of nonionic surface active agents in machine dishwashing is as a rinse additive. If completely satisfactory performance in auto-

matic machines is to be obtained, the use of a rinse additive is required. Rinse additives result in quicker and more complete draining and drying of utensils and glassware, reduction in or freedom from so-called "water spots" and filming on utensils and glassware, and a brighter and cleaner appearance of all washed items.

In the newer and more expensive automatic dishwashing machines, a separate ejector is provided for the rinse additive which is ejected into the machine during a rinse cycle. However, the older machines and most of the lower and average priced newer machines do not have an ejector for the rinse additive. Accordingly, in these machines it is necessary to add the rinse additive as an ingredient of the automatic dishwashing composition or to stop the machine and add the rinse additive directly to the rinse cycle.

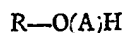
In copending application No. 28813/66 (Serial No. 1,131,333), a certain group of alkylene oxide condensation products are disclosed and claimed, as useful rinse additives for automatic dishwashing machines. These additives are employed along with a typical machine dishwashing composition, i.e., one containing a surface active agent and various inorganic salts, either by means of a separate ejector by stopping the machine as described above.

Accordingly, it is an object of the present invention to provide new nonionic condensation products which are useful as surface active agents and as rinse additives in automatic dishwashing machines. It is a further object of the present invention to provide products which, when employed in automatic dishwashing machines suppress foam generation at temperatures as low as 100° F. Still another object of the invention is to provide products which may be employed as the sole surface active agent in automatic machine operations, thereby functioning as wetting agent, foam

[Price 4s. 6d.]

suppressant and rinse additive. A further object of the invention is to provide novel automatic dishwashing compositions.

The novel condensation products of the present invention are prepared by the condensation of an essentially linear primary aliphatic alcohol having from ten to eighteen carbon atoms in the aliphatic chain, or, preferably, a mixture of such alcohols, with a critical amount of a mixture of ethylene oxide and propylene oxide. The products of the present invention are the products obtained by condensing, on a weight basis, 20% to 45% alcohol, 30% to 55% propylene oxide, and 20% to 35% ethylene oxide. These products are a cogenetic mixture of heteric compounds of the general formula:



in which R represents an essentially linear alkyl group having from ten to eighteen carbon atoms, with the proviso that R in at least 70 weight percent of said compounds in said mixture has from twelve to sixteen carbon atoms, and

A represents a random mixture of oxypropylene and oxyethylene groups, said oxypropylene and oxyethylene groups being from 55% to 80% of the total weight of the compounds, the oxypropylene to oxyethylene ratio of said total weight being from 0.85:1 to 2.75:1. The R—O in the foregoing formula may also be defined as the residue of the alcohol or alcohol mixture employed in the condensation reaction, i.e., the alcohol or alcohol mixture with the hydrogen of the OH radical removed.

The term "cogenetic mixture", as used herein, designates a series of closely related homologues that are obtained by condensing a plurality of oxide units with an alcohol or a mixture thereof. (See U.S. Patent No. 2,549,438, particularly column 2, line 40 et seq.) As is known when a mixture of compounds of this type is generated, various oxyalkylene chain lengths are obtained. Accordingly, throughout this specification when oxyalkylene weight percents are referred to, average weight percents are meant.

The crux of the present invention is the discovery that products possessing exceptional surface active and rinse additive properties can be prepared by employing critical amounts of certain alcohols and of certain mixtures of ethylene oxide and propylene oxide. Only by employing certain amounts of these reactants may products be prepared with (1) have the ability to remove oily film from hard surfaces such as dishes and flatware; (2) provide low surface tension and good wetting action in very dilute aqueous solutions without generating foam under severe agitation; (3) suppress foam generated by residues of natural soils, such as dried milk and egg, even at temperatures of 100° F.; (4) cause the washing solu-

tion to "sheet" off glass or ceramic surfaces without leaving water droplets, and (5) are sufficiently water-miscible to rinse easily off the washed surfaces without leaving an oily film.

Alcohols which may be employed in the preparation of the products of the present invention are those essentially linear primary aliphatic alcohols having from ten to eighteen carbon atoms. However, at least 70 weight percent of the alcohol reactant should comprise an alcohol or mixture of alcohols having from twelve to sixteen carbon atoms. Mixtures of alcohols are preferred since their use provides for a good balance of properties in the resulting products. Branched chain aliphatic alcohols are not operable in this invention, nor are aliphatic alcohols containing less than ten carbon atoms in the aliphatic chain since these alcohols do not impart biodegradability to the resulting products, nor do the products resulting from their use, along with the stated amounts of oxides, possess good surface active or rinse additive properties. Examples of suitable alcohols include decyl alcohol, undecyl alcohol, lauryl alcohol, tridecyl alcohol, tetradecyl alcohol, pentadecyl alcohol, cetyl alcohol, heptadecyl alcohol, stearyl alcohol, hydrogenated tallow alcohol, and mixtures thereof. They may be naturally-derived, such as from coconut oil, or synthetically-derived, such as from linear alkanes or linear olefins. It is possible to employ small amounts of branched chain alcohols along with the above-mentioned linear alcohols as long as the amount used does not impair the biodegradability of the resulting product. An example of such an alcohol mixture is commercially available from Shell Oil Company under the name NEODOL 25 (a mixture of  $C_{12}$ — $C_{14}$  alcohols).

To be useful in the present invention, the alcohol reactant must contain only the number of carbon atoms discussed above and then only in the amounts stated. These variables are important in order to obtain products having the desired balance of biodegradability, hydrophobicity, water-miscibility and activity. For the same reasons, the amounts of ethylene oxide and propylene oxide which may be employed in the present invention are extremely critical. It has been determined that products prepared employing amounts of reactants outside of the ranges of the present invention do not possess the outstanding properties of the products of the present invention.

The products of this invention are prepared by condensing an alcohol or mixture of alcohols, as described above, with a mixture of ethylene oxide and propylene oxide. The oxide mixture may be added to the alcohol in one continuous step or it may be added in several steps. If the oxide mixture is added in several steps, it is not necessary that the amount of ethylene oxide and propylene oxide

added in each step be within the required weight and ratio ranges. It is only necessary that the total amount of ethylene oxide and propylene oxide added constitute 55% to 80% by weight of the product and that the ratio of the total amount of propylene oxide to the total amount of ethylene oxide be in the range of 0.85:1 to 2.75:1. Thus, it is possible to add a first amount of oxide mixture which has more ethylene oxide than propylene oxide as long as subsequent amounts of oxide mixture added bring the total amount of oxides added within the required ranges.

The products of this invention have a heteric structure. By this is meant that the products possess random distribution of oxyethylene and oxypropylene groups. As mentioned above, the amount of oxides used is very important. In order to obtain the products of this invention, it is important that the oxides be employed in a weight ratio of propylene oxide to ethylene oxide of from 0.85:1 to 2.75:1, preferably 1.25:1 to 2.25:1. Not only is it important that the ratio of propylene oxide to ethylene oxide be maintained within the above-stated range, but also it is important that the total amount of oxides employed be such that the products contain from 55% to 80% by weight of oxyethylene and oxypropylene groups.

The products of this invention may generally be prepared by condensing the alcohol with a mixture of ethylene oxide and propylene oxide in the presence of an alkaline catalyst. Catalysts which may be employed include sodium hydroxide, potassium hydroxide, sodium ethylate, sodium methylate, potassium acetate, sodium acetate and trimethylamine. Any other types of catalysts commonly used for alkylene oxide condensation reactions may also be employed.

After the condensation reaction is completed, the catalyst is removed from the reaction mixture by any known procedure such as neutralization and filtration, or ion exchange. The condensation is preferably carried out at elevated temperatures and pressures.

The invention also provides an automatic dishwashing composition comprising an inorganic salt, an alkaline builder, a chlorinated inorganic compound and a cogeneric mixture of heteric compounds of the invention.

The following Examples illustrate the invention. All parts are by weight unless otherwise stated.

#### EXAMPLE I

A clean, dry, reaction vessel equipped with a stirrer, thermometer, inlet tube, pressure gage and heat exchange means was purged with nitrogen and then charged with two parts of potassium hydroxide and 500 parts of a mixture of  $C_{12}$ — $C_{15}$  alcohols having an average molecular weight of 207. The charge was heated to about 140° C. and with good stirring a mixture of 1000 parts of propylene

oxide and 500 parts of ethylene oxide (weight of mixture being 75% of total, propylene oxide to ethylene oxide ratio of 2:1) was added at such a rate as to keep the pressure below 90 psig. The total addition time was about five hours. The reaction mixture was stirred for an additional hour at 135° C. to complete the reaction, cooled to 50° C., and removed from the vessel. The catalyst was neutralized with glacial acetic acid and volatiles were removed by stripping at about 100° C. and 10 mm pressure for one hour. The product is a light yellow, biodegradable liquid having a molecular weight by hydroxyl number of 796 and a cloud point (1% solution) of 26° C. Biodegradability was determined by the shake flask culture technique. This involves first preparing a basal medium of distilled water, yeast extract, ammonium chloride, potassium hydrogen phosphate, magnesium sulfate septahydrate, potassium chloride and ferrous sulfate and then adding a candidate nonionic condensation product (in the form of a solution) to the basal medium to give a nonionic concentration of 30 ppm. A microbial culture is prepared based on unchlorinated final effluent from an activated sludge plant. The basal medium containing the candidate nonionic is then inoculated with the microbial culture and placed in a shaking machine for aeration. To follow the course of biodegradation, aliquots are removed for analysis (potassium iodobismuthate method) immediately after inoculation and at 24-hour intervals thereafter for a period of seven days. The analysis indicates the amount of nonionic remaining in parts per million. Although there is uncertainty in the art as to that which is biodegradable and that which is not sufficiently biodegradable, for the purpose of this application a nonionic which degrades 85% within seven days is considered biodegradable.

#### EXAMPLE II

Following the procedure of Example I, 621 parts of a mixture of  $C_{12}$ — $C_{15}$  alcohols having an average molecular weight of 207 was condensed with a mixture of 828 parts of propylene oxide and 621 parts of ethylene oxide (weight of mixture being 70% of total, propylene oxide to ethylene oxide ratio of 1.33:1). The product, a light yellow, biodegradable liquid, had a hydroxyl number of 86.9 and a cloud point (1% solution) of 25° C.

#### EXAMPLE III

Following the procedure of Example I, 640 parts of a mixture of  $C_{12}$ — $C_{15}$  alcohols having an average molecular weight of 207 was condensed with a mixture of 860 parts of propylene oxide and 500 parts of ethylene oxide (weight of mixture being 68% of total, propylene oxide to ethylene oxide ratio of 1.72:1). The product, a light yellow, biodegradable liquid, had a hydroxyl number of 90.2 and a cloud point (1% solution) of 18° C.

## EXAMPLE IV

102 14, 19

5 A clean, dry, reaction vessel equipped as in Example I was purged with nitrogen and then charged with two parts of potassium hydroxide and 500 parts of an alcohol mixture containing approximately 40% of a  $C_{12}$  alcohol, 30% of a  $C_{14}$  alcohol, 20% of a  $C_{16}$  alcohol and 10% of a  $C_{18}$  alcohol. The charge was heated to about 150° C. and with good stirring, a mixture of 1000 parts of propylene oxide and 500 parts of ethylene oxide (weight of mixture being 75 % of total, propylene oxide to ethylene oxide ratio of 2:1) was added at such a rate as to keep the pressure below 90 psig.

10 The total addition time was about four hours.

15 The reaction mixture was stirred for one hour at 150° C. to complete the reaction, cooled to 50° C., and removed from the vessel. The catalyst was neutralized with glacial acetic acid and volatiles were removed by stripping at 100° C. and 10 mm pressure for one hour.

20 The product is a light yellow, biodegradable liquid having a hydroxyl number of 69 and a cloud point (1% solution), of 25° C.

## EXAMPLE V

25 Following the procedure of Example IV, 440 parts of an alcohol mixture containing approximately 65% of a  $C_{12}$  alcohol, 26% of a  $C_{14}$  alcohol and 9% of a  $C_{16}$  alcohol was condensed with a mixture of 1040 parts of propylene oxide and 520 parts of ethylene oxide (weight of mixture being 78% of the total, propylene oxide to ethylene oxide ratio

102 19, 14

30

of 2:1). The product, a light yellow, biodegradable liquid, had a hydroxyl number of 65 and a cloud point (1% solution) of 29° C.

35

## EXAMPLE VI

The products prepared in the previous examples were employed in automatic dishwashing machines in the following manner.

40

Several dishwashing compositions were formulated from tetrasodium polyphosphate, sodium tripolyphosphate, sodium metasilicate, chlorinated trisodium phosphate and various nonionic surface active agents. Each composition containing approximately three weight percent of surface active agent is tested in a 1965 "Kitchen Aid" Dishwasher as follows.

45

The dishwasher is loaded with dishes, glasses and silverware. Twenty parts of the candidate composition is then added to the machine. The wash cycle is begun using water at a temperature of 100° F. Prior to the end of the wash cycle, the dishwasher is turned off and the height of the foam above the water level is measured. The same test is conducted two additional times, once adding twelve parts of powdered milk to the machine prior to the start of the wash cycle and once adding fifteen parts of fresh egg to the machine prior to the start of the wash cycle. Throughout the tests, the temperature is maintained around 100° F. Upon completing the tests, the washed items are inspected for cleanliness.

50

55

60

The results of the tests are presented in Table 1.

65

102 23, 24, 27-29

103 25, 30

TABLE 1

Foam Tests at 100° F.

Foam Height, Inch.

Surface Active Agent	No Soil	Milk Soil	Egg Soil	Comments
1. Product of Example I	1/8	3/8	5/8	All items washed appeared clean, without spots, streaks or films.
2. Product of Example II	1/4	1/2	1	" "
3. Product of Example III	1/8	1/2	3/4	" "
4. Product of Example IV	1/8	3/8	3/4	" "
5. Product of Example V	1/8	3/8	3/4	" "
6. A	1/4	1/2	1—1/2	Oily film on all items washed.
7. B	overflowed	overflowed	overflowed	Streaking and spots on all items washed.
8. C	overflowed	overflowed	overflowed	Streaking and spots on all items washed.
9. D	overflowed	overflowed	overflowed	Streaking and spots on all items washed.

A —Condensation product of a mixture of C<sub>12</sub>—C<sub>15</sub> alcohols having an average molecular weight of 207 and a mixture of ethylene oxide and propylene oxide, the total weight of the oxide mixture being 50% of the product, the ratio of oxypropylene to oxyethylene in said mixture being 1:1.

B —Condensation product of a mixture of C<sub>12</sub>—C<sub>15</sub> alcohols having an average molecular weight of 207 and a mixture of ethylene oxide and propylene oxide, the total weight of the oxide mixture being 75% of the product, the ratio of oxypropylene to oxyethylene in said mixture being 0.5:1.

C —Condensation product of ethylene oxide and nonylphenol, the product being 70% by weight oxyethylene groups.

D —Condensation product of a mixture of fatty alcohols (C<sub>12</sub>—C<sub>18</sub>) and ethylene oxide, the product being 70% by weight oxyethylene groups.

From the results presented in Table 1, it is clear that only those products of the present invention were successful in suppressing the foam at 100° F. and in providing for unstreaked and unspotted smooth surfaces on the items washed. Agents A and B are products similar to those of the present invention differing, in one case, in the total oxyalkylene content and, in the other, in the oxypropylene to oxyethylene ratio. Agents C and D are well-known nonionics which have been employed in automatic dishwashing formulations.

#### EXAMPLE VII

The products of Examples I—V were tested as rinse additives employing a "Kitchen Aid"

Dishwasher at operating conditions of 100° F. in the following manner.

After a loaded machine had completed the wash cycle and the first rinse cycle, 0.8 part of the candidate rinse additive was added to the machine. After the rinse cycle was completed, the amount of foam present in the machine was observed. The machine was then allowed to complete the drying cycle and the washed items were observed under infrared for spots or films. Tests were concluded when the items observed were substantially spotted or filmed or, if they remained essentially unspotted and unfilmed, for twelve complete dishwashing cycles. The results of the tests are presented in Table 2.

TABLE 2

## Rinse Additive Tests

Rinse Additive	Foam Height, Inch	Spotting or Filming
Product of Example I	nil to 1/8	*
Product of Example II	1/8	*
Product of Example III	1/8	*
Product of Example IV	1/8	*
Product of Example V	1/8	*

\*No film; occasional spot on some glasses.

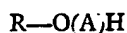
## EXAMPLE VIII

An automatic dishwashing composition was prepared as described in Example VI employing three weight percent of the product of Example I. The composition was employed in a "Kitchen Aid" Dishwasher loaded with dishes, glasses and silverware. The dishwasher was allowed to complete its washing, rinsing and drying cycles at 100° F., stopping it only to measure the foam height, as in the previous examples. The same test was carried out adding a milk soil and an egg soil. The same foam height results that are reported in Table I were obtained. After completing the tests, the items washed were observed for spotting and filming. No spotting or filming was observed.

This example demonstrates that the use of a composition containing a product of the present invention in automatic dishwashing machines suppresses foam, provides for good wetting action and results in dishes, glasses, and silverware free from oily film and water spots, even without the addition of a separate rinse additive.

## WHAT WE CLAIM IS:—

1. A cogenetic mixture of heteric compounds of the general formula:



in which R represents an essentially linear alkyl group having from ten to eighteen carbon atoms, with the proviso that R in at least 70 weight percent of said compounds in said mixture has from twelve to sixteen carbon atoms, and

A represents a random mixture of oxypropylene and oxyethylene groups, said oxypropylene and oxyethylene groups being from 55% to 80% of the total weight of the compounds, the oxypropylene to oxyethylene ratio of said total weight being from 0.85:1 to 2.75:1.

2. A mixture according to Claim 1, wherein

R is derived from a mixture of  $C_{12}$ — $C_{15}$  alcohols.

3. A mixture according to Claim 1 or 2, wherein the oxypropylene to oxyethylene ratio is from 1.25:1 to 2.25:1.

4. A process for the preparation of a cogenetic mixture of Claim 1, which comprises condensing a mixture of essentially linear primary aliphatic alcohols having from ten to eighteen carbon atoms in the aliphatic chain, said mixture comprising at least 70 weight percent of alcohols having from twelve to sixteen carbon atoms, with a mixture of ethylene oxide and propylene oxide in a weight ratio of propylene oxide to ethylene oxide of from 0.85:1 to 2.75:1, the total weight of the compounds being from 55% to 80% oxyethylene and oxypropylene groups.

5. An automatic dishwashing composition comprising an inorganic salt, an alkaline builder, a chlorinated inorganic compound and a cogenetic mixture of heteric compounds as claimed in Claim 1, 2 or 3.

6. A mixture in accordance with Claim 1, substantially as described in foregoing Example I.

7. A mixture in accordance with Claim 1, substantially as described in foregoing Example II.

8. A mixture in accordance with Claim 1, substantially as described in foregoing Example III.

9. A mixture in accordance with Claim 1, substantially as described in foregoing Example IV.

10. A mixture in accordance with Claim 1, substantially as described in foregoing Example V.

11. A method in accordance with Claim 4, substantially as described in foregoing Example I.

12. A method in accordance with Claim 4, substantially as described in foregoing Example II.

13. A method in accordance with Claim

45

50

55

60

65

70

75

80

85

- 4, substantially as described in foregoing Example III.
14. A method in accordance with Claim 4, substantially as described in foregoing
- 5 Example IV.
15. A method in accordance with Claim 4, substantially as described in foregoing Example V.
- 10 16. A composition in accordance with Claim 5, substantially as described in foregoing Example VI.
17. A composition in accordance with Claim 5, substantially as described in foregoing Example VIII.
- FORRESTER, KETLEY & CO.,  
Chartered Patent Agents,  
Jessel Chambers, 88/90, Chancery Lane,  
London, W.C.2.  
and  
Rutland House, Edmund Street,  
Birmingham 3.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.  
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which  
copies may be obtained.